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ORIGINAL PAPER

Impact of ionizing radiation on the properties of a hydrobiodegradable aliphatic-aromatic copolyester

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Abstract. This paper presents the results of the studies on changes of selected quality parameters of hydrobiodegradable aliphatic-aromatic copolyester (AAC). Radiation treatment was performed at the Institute of Nuclear Chemistry and Technology in Warsaw, using cobalt gamma-ray sources "Issledovatel" (dose rate 0.389 Gy/h) and "GC 5000" (8.5 Gy/h). The material was subjected to the impact of radiation doses of 5, 10, 20 and 40 kGy. Selected parameters of the packaging material, important from the standpoint of a potential application, have been studied: gaseous products of radiolysis, strength parameters in accordance with PN EN ISO 527-3, global migration PN-EN-1186-1:2002, FT-IR analysis using PCA method, contact angle measurement using the drop shape method. The results have demonstrated that there is no significant influence of ionizing radiation on AAC film parameters. Correlation between doses applied and values of measurements has not been found.

Key words: aliphatic-aromatic copolyester • biodegradable polymer • ionizing radiation

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Introduction

One of the main factors determining the market success of the product is its packaging – it ensures the quality parameters on the way from the production line down to the consumer, and it is one of the most important marketing tools [1, 4]. In case of the products sterilized with ionizing radiation, the packaging is an integral part of the technology. Currently, the radiation sterilization uses industrial sources of radiation such as: electron, gamma and X-ray. It is worth mentioning, in the year of celebrations of the 100th anniversary of Maria Skłodowska-Curie's Chemistry Nobel Prize, that she published the first paper on the impact of X-rays on bacteria. In this scope, it can be concluded that this scientist was a precursor of radiation sterilization methods.

Radiation sterilization has found application for medical devices, food, herbs and spices, surgical implants, pharmaceuticals and cosmetics [2]. The originality of using radiation to battle the pathogens is that the material is sterilized in the entire volume at room temperature and packed, while eliminating the risk of secondary contamination.

The maintenance of the specific product characteristics, given in the process of radiation and protection against secondary contamination requires using of an appropriate packaging, which must also meet the requirements of the radiation treatment. In addition to ionizing radiation resistance, the packaging should not

have harmful effects on the packaged product, which is especially important for food packaging, medical equipment and materials. The basic requirements for packaging under the influence of radiation are: maintaining the required mechanical performance, lack or keeping within an acceptable range the migration of chemicals, and maintaining the aesthetic qualities (e.g. dyeing, printing, transparency).

From the environmental point of view, packagings are the least effective form of use of plastics. A short shelf life and the vast mass of packaging lead to rapid exploitation of fossil fuel stocks, especially oil and natural gas. The diversity of composition and form of packaging, the presence of impurities and economic conditions, make the packaging waste management one of the most serious problems of modern civilization.

The connection of two modern technologies in one product: radiation preservation and biodegradable packaging, involves the possibility of creating a modern, innovative product that will provide high quality and health safety for the consumer, with a low environmental impact of packaging waste. Such a combination could be an interesting alternative for the growing group of consumers, who value high quality product, while being environmental friendly.

Prior to consider specific applications of the packaging material, is to understand its behaviour under the influence of ionizing radiation, in particular changes in the characteristics, essential from the packaging point of view, depending on: radiation dose, source used and process parameters.

The combination of knowledge, experience and research effort of specialists in the field of radiation treatment and packaging science, allows for comprehensive evaluation of the test material for a potential application of real products packaging.

For this purpose, the results of typical packaging materials tests with the results of chemical analysis of gaseous products of radiolysis were compared. The latter, based on previous knowledge in the field of polymer radiation chemistry, allow to preevaluate the radiation resistance of polymer material.

Materials tested

The subject of the research was a film based on aliphatic-aromatic copolyester (AAC) provided by Cortec Company. It is fully biodegradable according to DIN EN 13432:2000-12 standards. The film tested was hazy white, with a thickness of 0.076 mm and a density of 1.2–1.5 g/cm^3.

The aromatic compounds exhibit exceptional resistance to ionizing radiation. For example, the capacity of hydrogen emitted from polypropylene during radiation process is about 100 times smaller than that of polystyrene. In addition, the protective effect of aromatic compounds in radiation organic chemistry is well known. Aromatic rings, through the phenomenon of energy and charge transfer, are able to dissipate part of the radiation energy absorbed by the adjacent aliphatic mers. Based on the literature data and our previous experience, a relatively good radiation resistance of AAC is expected.

Sample irradiation

The irradiation process was conducted at the Institute of Nuclear Chemistry and Technology (INCT) in Warsaw. Samples to test mechanical properties were irradiated in a gamma radiation source GC 5000 of Indian production with a dose rate of 8.5 kGy/h. In order to compare the impact of dose on the effects of post radiation oxidation, the film had been additionally exposed to cobalt source of gamma radiation – Issledovatel – with a dose rate of 0.389 kGy/h and the electron beam accelerated by a linear electron accelerator of Russian production of "Elektronika" 10/10 with an energy of 10 MeV and beam power of 10 kW. All the equipment for radiation modification of materials are certified by the Accredited Laboratory for Measurements of Technological Doses.

In research, the following radiation doses have been used: 0, 5, 10, 20 and 40 kGy. The selection of radiation doses was derived from the radiation applications described in the literature, stemming from legal regulations as well as from the range of doses practically applied [8].

The study of material properties

Performance of hydrogen release and oxidation

In the analysis of radiolysis gaseous products a Shimadzu 2014 gas chromatograph (made in Japan) was used, with the extension of thermal conductivity detector (tcd-2014) and a column packed – molecular sieve 5 A. Using gas chromatography (GC), the performance of evolved hydrogen (GH_2) and absorbed oxygen (GO_2) were determined. Performance of hydrogen formed by the ionizing radiation allows to assess the number of originally generated macro-radicals. Loss of oxygen is associated with the process of radiation-induced oxidation of polymer material. The relationship between the results of chromatographic analysis and the mechanical properties of packaging material, subjected to radiation, were studied.

Mechanical parameters

Basic strength parameters were determined for the film samples, subjected to the radiation doses mentioned above. These parameters decide about film's possible packaging applications. The parameters were: tensile stress and elongation at break. The measurements were based on PN-EN ISO 527:1998, using INSTRON 5565 tensile testing machine. The samples subjected to break had a width of 15 and 50 mm working section. The speed of the jaws was 200 mm/min.

Global migration

Mass measurement of the non-volatile substances, migrating from the test material to the model solution, was made in accordance with the guidelines of PN-EN-1186-1:2002 specification. Two contacting

media as food simulants were used: water and ethyl alcohol (96%). Simulation of contact with food products was performed by a 10-day full immersion at 40°C. Global migration was measured by weight, in five replications.

Analysis of IR spectra with principal component analysis (PCA) method

A series of spectra were performed using a Fourier transform infrared spectrometers of Perkin Elmer Spectrum 100. PCA analysis of the obtained spectra was performed using the Unscrambler 9.7 program. PCA is an initial method of exploratory analysis, which allows the detection of a data structure. PCA is the data size reducing method, which allows visualizing the structure, while preserving maximum information in a multidimensional data set [7].

Measurement of contact angle

The measurement of water contact angle for the films tested has been carried out with a TRACKER device (manufactured by I. T. Concept, France). Tested films were placed under the camera, connected to a computer and then a water drop was put using a syringe. To carry out the test, ultra-pure water was used, obtained from the ELGA PURELAB water purification system. The measurement has been conducted in the environment of 20°C.

Results and discussion

Chromatographic studies

As expected, the efficiency of hydrogen release caused by ionizing radiation (0.025–0.028 mol/J) is characteristic of the radiation-resistant polymers. For example, for polyethylene, this value is estimated as 0.25–0.30 μmol/J, depending on the type of material. Figure 1 shows the dependence of GH_2 as a function of radiation dose. GH_2 value is practically constant in the range of doses tested (5–40 kGy) and changes a little with increasing rate of radiation dose. Figure 3 shows the dependence of the volume of hydrogen formed by radiolysis of 1 g of polymer as a function of radiation

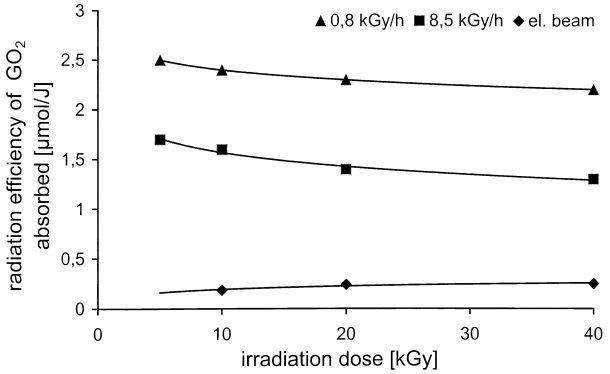

Fig. 1. Radiation efficiency of hydrogen evolved GH_2 (μmol/J).

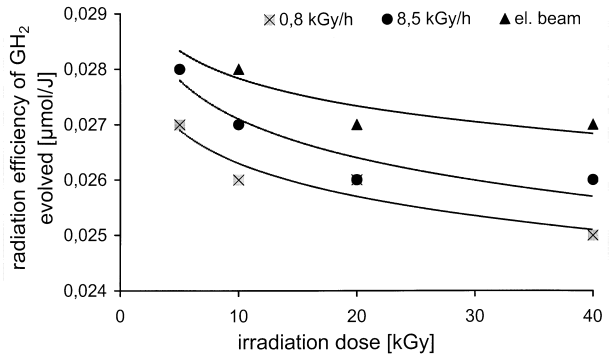

Fig. 2. Radiation efficiency of oxygen absorbed GO_2 (μmol/J).

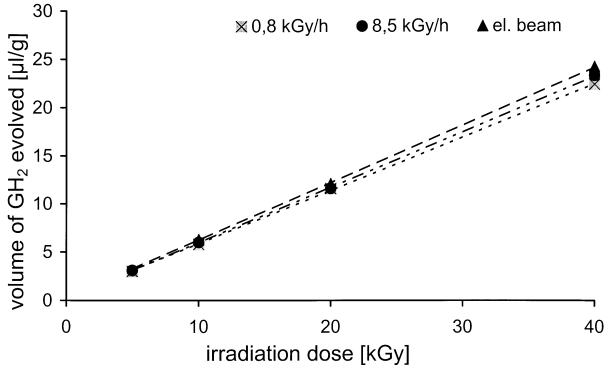

Fig. 3. The volume of hydrogen evolved (μl/g).

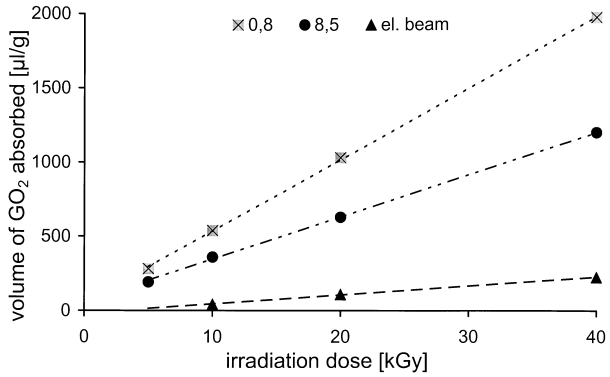

Fig. 4. The volume of oxygen absorbed (μl/g).

dose. There is, however, a very significant impact of dose rate on the process of after-radiation oxidation, highlighted in size of oxygen absorbed by the film. Figure 4 describes the dependence of the volume of oxygen absorbed by 1 g of the polymer during irradiation as a function of dose. This is clearly visible, especially when compared to electron beam radiation treatment and gamma radiation. High dose rate significantly restricts the access of oxygen into the polymer by diffusion. The slight decrease in the oxidation efficiency (Fig. 2) with level of gamma radiation dose is connected with a progressive consumption of oxygen in the bottle with the polymer. Figure 4 shows the dependence of efficiency of oxygen absorbed as a function of the dose absorbed by 1 g of polymer.

For electron beam radiation dose, modification and thus prolongation of irradiation slightly increases the efficiency of oxidation. GH_2 measurements, intermediate between the 0.025–0.029 values characteristic

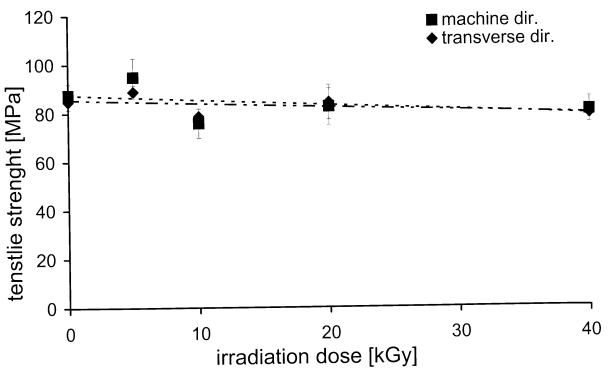

Fig. 5. Change of tensile stress as a function of radiation dose.

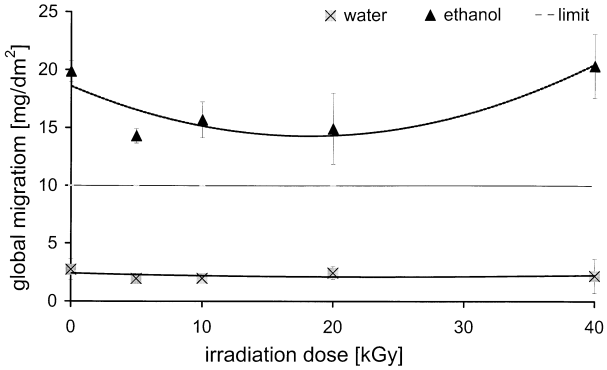

Fig. 6. Global migration for doses tested.

of aromatic and aliphatic compounds, confirm the presence of the protective effect. The extent of this phenomenon depends on the relationship between the mass participation of aromatic and aliphatic compounds in the material and forms of their contact.

Mechanical properties

Transformation of the internal structure of the polymer causes many changes in the parameters of irradiated material. As far as packaging applications are concerned, the mechanical parameters are extremely important. For tested material, there were no changes in breaking stress with increasing doses of radiation (Fig. 5). In the range of radiation doses used, the observed changes do not exceed 13% of the initial value. It allows to use this film for wrapping of goods that need radiation sterilization. Minor changes in this regard make that no changes are required to the parameters of the packaging and its design, in relation to the solutions used for products which do not undergo irradiation.

Also, the flexibility of the polymer is connected directly to its structure. The lowest dose used (5 kGy) caused a small decrease in this parameter. For the radiation doses of 20 and 40 kGy, there is a visible increase in elongation at break, up to 30% higher compared to non-irradiated samples (Table 1). This may indicate that the gamma radiation cause cross-linking processes rather than degradation in this film.

Significant changes are taking place in an identical extent for the parameters measured in both directions, suggesting a uniform effect of radiation on all elements of the structure of the polymer, regardless of their location and configuration. The direction and intensity of the recorded changes demonstrates a strong similarity to other biodegradable materials with similar composition [5, 6].

Table 1. Elongation at break values for various radiation doses

Dose (kGy)	Elongation at break (%)	
	Machine direction	Transverse direction
0	91.35 ± 46.00	76.23 ± 12.68
5	41.47 ± 24.29	39.87 ± 26.57
10	89.30 ± 39.25	52.78 ± 33.32
20	113.80 ± 31.49	92.39 ± 36.79
40	63.33 ± 45.22	38.12 ± 12.68

Global migration

Results of global migration measurements demonstrate no influence of ionizing radiation with the tested doses on value of global migration to water (Fig. 6). Global migration to ethanol of the tested material (both irradiated and non-irradiated) is over the limit (10 mg/dm^2). Irradiation doses up to 20 kGy shows, however, lower values that material irradiated with 40 kGy. This can be explained by the cross-linking processes, occurring with lower doses, which hinder the movement of low-molecular compounds. Although the global migration to ethanol exceeds the limit contained in the Directive [3], it does not disqualify the test material. In addition, changes in the migration process demonstrate that the dose range 5–40 kGy does not increase values of global migration even with ethanol, a good solvent, with much higher extraction capacity of the low molecular organic compounds than most food products. This leads to the conclusion that radiation of the test materials, used in the experimental group, does not result in increased migration.

Thus, materials with certificates allowing for contact with food products in the field of migration may be a sufficient guarantee for the safety of packaging material in the above conditions.

IR analysis with principal component analysis (PCA) method

PCA analysis was performed for IR spectra data, measured in the range from 4000 to 400 cm^{-1}. The charts set by the first two components PC1 and PC2 are presented. A clear grouping of similar samples in terms of structure of the whole spectrum can be observed, but the distribution of points relative to the first component PC1 is not correlated with the dose of radiation (Fig. 7). Therefore, it can be concluded that the magnitude of change in the structure does not change proportionally to the dose, which was confirmed by our other studies. The first and second main component explained the variability successively in 71 and 16%.

Measurement of surface contact angle

The wettability of solids plays a very important practical role in many industrial processes such as: apply-

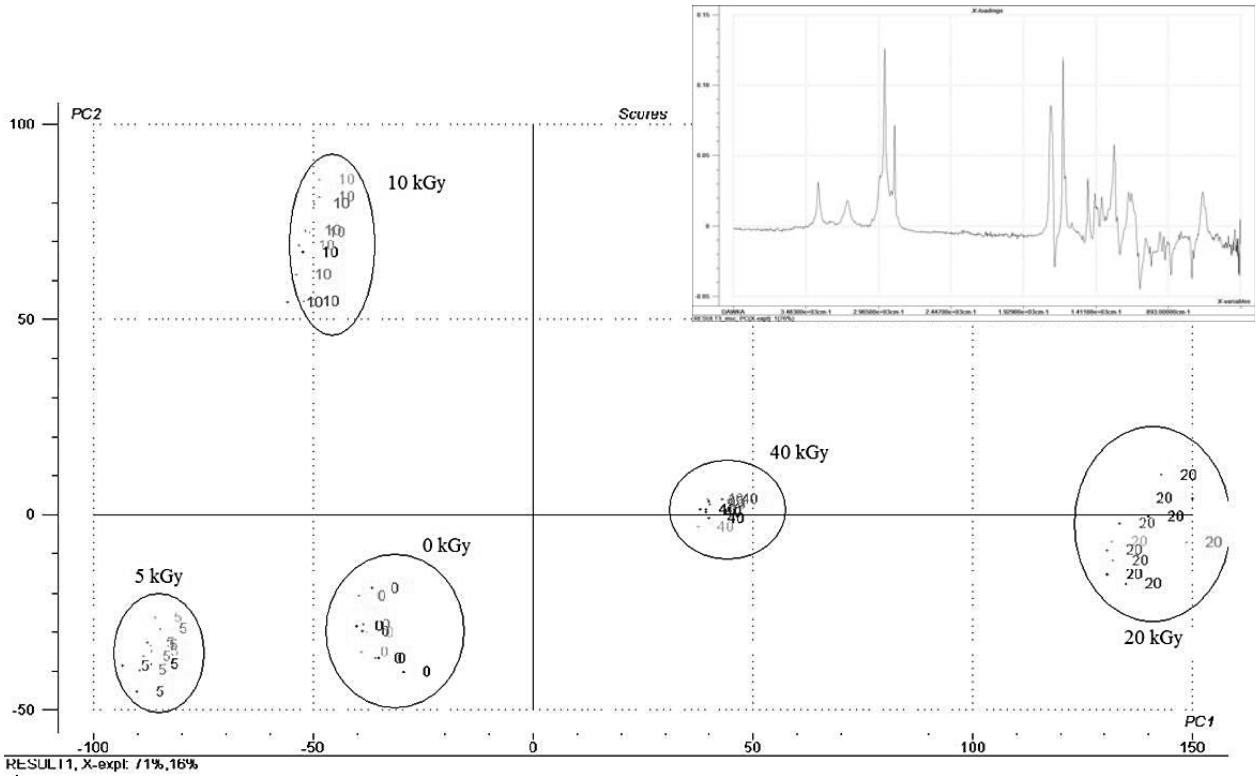

Fig. 7. Principal component analysis for AAC film before and after irradiation .

ing a protective coating, lubrication, adhesion, and printing. This parameter is important in assessment of the adhesive properties of polymers in the solid state and in the analysis of the effects of surface layer modification of polymeric materials [9].

Changes in the polymer structure (confirmed by IR spectra analysis and determination of the volume of hydrogen evolved during exposure to radiation) suggest that the major degradation changes in the non-polar hydrocarbon chain occur after 10 kGy irradiation, which is also reflected by the increase in surface hydrophobicity (Fig. 8).

Conclusions

The subject of the research was a film based on an aliphatic-aromatic copolyester (AAC) provided by Cortec Company. The material was subjected to γ-radiation, coming from a cobalt bomb "Issledovatel". Doses of 5, 10, 20 and 40 kGy were applied. Performance of hydrogen release showed that GH_2 value is practically constant in the range of doses tested. Results of basic strength parameters showed no significant differences in breaking stress values between both test directions. Radiation used in the experiment does not result in increased global migration. There is no evidence to limit the contact of the test material subjected to exposure to the above radiation doses with water or dry products. It can be concluded that the magnitude of changes in the structure does not change proportionally to the dose, which was confirmed by other studies like principal component analysis methods. PCA have determined that the size and direction of changes in the material is not dependent on the exposed dose as well as the changes are not specific to just one area. Ionizing radiation strongly affects the changes of the surface wettability. Significant differences were observed in value of the test material contact angle, however no correlation between the contact angle and the dose was found.

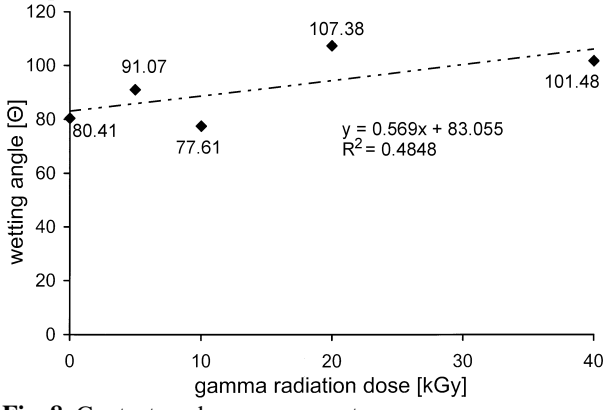

Fig. 8. Contact angle measurement.

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References

1. Ankiel-Homa M, Czaja-Jagielska N, Assman K (2011) Key aspects of packaging design process. Opakowanie 7 (in Polish)
2. Chmielewski AG, Haji-Saeid M, Ahmed S (2005) Progress in radiation processing of polymers. Nucl Instrum Methods Phys Res B 236:44–54

3. Directive 1999/2/EC of the European Parliament and of the Council of 22 February 1999 on the approximation of the laws of the Member States concerning foods and food ingredients treated with ionising radiation. OJ L 66, 13.3.1999, pp 16–23
4. Korzeniowski A, Ankiel-Homa M, Czaja-Jagielska N (2011) Innovations in packaging. Poznań University of Economics, Poznań (in Polish)
5. Melski K, Kubera H, Głuszewski W, Zimek Z (2007) Changes in selected biodegradation properties of packaging foils caused by ionizing radiation. Zeszyty Naukowe Akademii Ekonomicznej w Poznaniu 93:7–23 (in Polish)
6. Melski K, Kubera H, Głuszewski W, Zimek Z (2011) Effect of ionizing radiation on the properties of PLA packaging materials. Nukleonika 56;1:65–69
7. Sikorska E (2008) Fluorescent methods in food analysis. Wydawnictwo Akademii Ekonomicznej w Poznaniu, Poznań, p 28 (in Polish)
8. WHO (1988) Food irradiation, a technique for preserving and improving the safety of food. World Health Organization, Geneva
9. Żenkiewicz M (2007) Analysis of the most important methods of investigations of polymeric materials' surface free energy. Polimery 52:10 (in Polish)